

# The origin of the anomalously strong influence of out-of-plane disorder on high- $T_c$ superconductivity

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## Abstract

The electronic structure of  $\text{Bi}_2\text{Sr}_{2-x}\text{R}_x\text{CuO}_y$  ( $R=\text{La, Eu}$ ) near the  $(\pi,0)$  point of the first Brillouin zone was studied by means of angle-resolved photoemission spectroscopy (ARPES). The temperature  $T^*$  above which the pseudogap structure in the ARPES spectrum disappears was found to have an  $R$  dependence that is opposite to that of the superconducting transition temperature  $T_c$ . This indicates that the pseudogap state is competing with high- $T_c$  superconductivity, and the large  $T_c$  suppression caused by out-of-plane disorder is due to the stabilization of the pseudogap state.

High temperature superconductivity occurs with doping carriers to a Mott insulator. Carriers are usually doped either by varying the oxygen content or by an element substitution. Unavoidably, these procedures introduce disorder that influences the superconducting transition temperature  $T_c$  even though only sites outside the  $\text{CuO}_2$  plane are chemically modified. For instance,  $T_c$  of the  $\text{La}_2\text{CuO}_4$  family depends on the size of the cation that substitutes for La,<sup>1</sup> and  $T_c$  of  $\text{Bi}_2\text{Sr}_{1.6}\text{R}_{0.4}\text{CuO}_y$  depends on the  $R$  element.<sup>2,3</sup> Recently, some of the present authors have studied extensively the  $\text{Bi}_2\text{Sr}_{2-x}\text{R}_x\text{CuO}_y$  system using single crystals and varied the  $R$  content  $x$  over a wide range for  $R=\text{La}$ ,  $\text{Sm}$ , and  $\text{Eu}$ .<sup>4</sup> The results clearly show that  $T_c$  at the optimal doping  $T_c^{\text{max}}$  depends strongly on the  $R$  element and decreases with the decrease in the ionic radius of  $R$ , in other words, with increasing disorder. By plotting  $T_c$  as a function of the thermopower at 290 K  $S(290)$ , it was found that the range of  $S(290)$  values for samples with a non-zero  $T_c$  becomes narrower with increasing disorder (see Fig. 1). Because  $S(290)$  correlates well with hole doping in many high- $T_c$  cuprates,<sup>5</sup> this suggests that the doping range where superconductivity occurs decreases with increasing out-of-plane disorder, in contrast to the naive expectation that the plot of  $T_c/T_c^{\text{max}}$  vs. doping would merge into a universal curve for all high- $T_c$  cuprates.

Despite the strong influence on  $T_c$  and on the doping range where superconductivity can be observed, out-of-plane disorder affects only weakly the conduction along the  $\text{CuO}_2$  plane. According to Fujita *et al.*,<sup>6</sup> out-of-plane disorder suppresses  $T_c$  more than Zn when samples with a similar residual resistivity are compared. This means that out-of-plane disorder influences  $T_c$  without being a strong scatterer, and that this type of disorder has an unexplained effect on  $T_c$ . To elucidate the reason of this puzzling behavior and why the carrier range of high- $T_c$  superconductivity is affected by out-of-plane disorder, we studied the electronic structure of  $R=\text{La}$  and  $\text{Eu}$  crystals by means of angle-resolved photoemission spectroscopy (ARPES) measurements. We particularly focused on the so-called antinodal position, the point where the Fermi surface crosses the  $(\pi,0)$ - $(\pi,\pi)$  zone boundary ( $\bar{\text{M}}$ -Y cut), due to the following reasons. It is generally accepted that in-plane resistivity is sensitive to the electronic structure near the nodal point of the Fermi surface.<sup>7,8,9</sup> The small influence of out-of-plane disorder on residual resistivity hence suggests that the electronic structure of this region is not much affected, as Fujita *et al.* mentioned.<sup>6</sup> Therefore, if out-of-plane disorder causes any influence on the electronic structure, it would be more likely to occur at the antinodal point of the Fermi surface.

The single crystals used in this study were grown by the floating zone method as reported previously.<sup>4</sup> As mentioned in that work and commonly observed for Bi-based high- $T_c$  cuprates, the composition of the grown crystal is not the same as the starting one and depends on the position within the boule. Accordingly, the hole doping level can not be determined from the starting composition of the crystal. On the other hand, it has been shown for many cuprates that  $S(290)$  correlates well with hole doping. Although  $S(290)$  is not directly related to the amount of carriers and should depend on the detail of the electronic structure, this empirical connection provides a reasonable indicator for the hole doping level. We note that we have confirmed in a separate experiment that the Fermi surface of a  $R=\text{La}$  and a  $R=\text{Eu}$  crystal with similar  $S(290)$  values coincided quite well,<sup>10</sup> implying that their hole doping was similar. Therefore, we use  $S(290)$  as a measure of doping in the following.<sup>11</sup>

All crystals were annealed at 750°C for 72 hours in air. The ARPES spectra were accumulated using a Scienta SES2002 hemispherical analyzer with the Gammadata VUV5010 photon source (He I $\alpha$ ) at the Institute of Solid State Physics (ISSP), the University of Tokyo, and at beam-line BL5U of UVSOR at the Institute for Molecular Science, Okazaki with an incident photon energy of 18.3 eV. The energy resolution was 10-20 meV for all measurements, which was determined by the intensity reduction from 90% to 10% at the Fermi edge of a reference gold spectrum. Thermopower was measured by a four-point method using a home-built equipment.  $S(290)$  was determined using crystals that were cleaved from those used for ARPES measurements except the  $R=\text{La}$  sample that had the largest doping in Fig. 4(a). For that particular sample, the  $S(290)$  value was estimated from the  $c$ -axis length deduced from x-ray diffraction based on the data shown in the inset to Fig. 1.

Figures 2(a) and (c) show the ARPES intensity plots along the  $(\pi,0)$ - $(\pi,\pi)$  direction at 100 K for  $R=\text{La}$  and Eu crystals that have a similar hole concentration. The samples were cleaved in situ at 250 K in a vacuum of better than  $5 \times 10^{-11}$  Torr. The  $S(290)$  values were 4.7  $\mu\text{V/K}$  and 4.8  $\mu\text{V/K}$  for the  $R=\text{La}$  and Eu samples, respectively, indicating that they are slightly underdoped (see Fig. 1). Figures 2(b) and (d) show momentum distribution curves (MDCs) of the  $R=\text{La}$  and Eu samples, respectively. We fitted the MDC curves to a Lorentz function to determine the peak position. The thus extracted dispersion is superimposed by white small circles on Figs. 2(a) and (c). The momentum where the dispersion curve crosses the Fermi energy  $E_F$  corresponds to the Fermi wave vector  $k_F$  on the  $(\pi,0)$ - $(\pi,\pi)$  cut, and

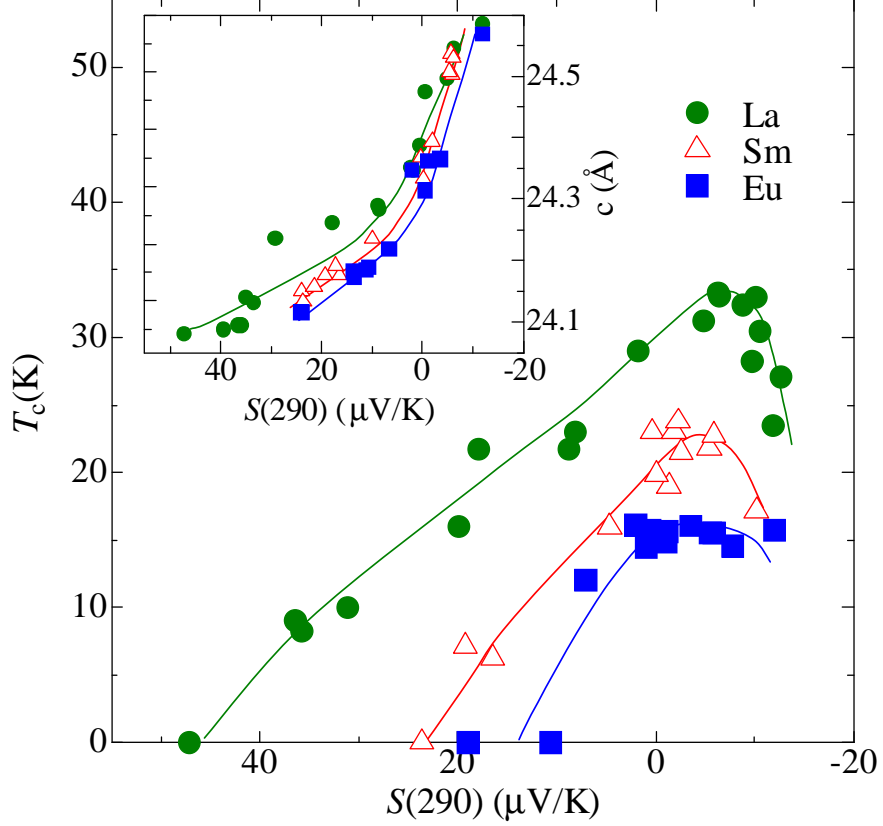


FIG. 1: (color online) The critical temperature  $T_c$  as a function of  $S(290)$ , the thermopower at 290 K.  $T_c$  was determined from the temperature dependence of resistivity, which was measured simultaneously with thermopower. Data are based on our previous work,<sup>4</sup> and some new data points are included. Inset: Lattice constant  $c$  plotted as a function of  $S(290)$ .

Fig. 2(e) shows the energy distribution curves (EDCs) of the two samples at  $k_F$ . Obviously, the  $R=\text{La}$  sample has a larger spectral weight at  $E_F$ , although the doping level of the two samples is very similar.

Figure 3 shows the EDCs of the two samples of Fig. 2 at various temperatures. To remove the effects of the Fermi function on the spectra, we applied the symmetrization method  $I_{\text{sym}}(\omega) = I(\omega) + I(-\omega)$ , where  $\omega$  denotes the energy relative to  $E_F$ .<sup>12</sup> As shown in Figs. 3(a) and (b), the symmetrized spectra of both samples show clearly a gap structure at the lowest measured temperature, 100 K. Because we are probing the antinodal direction at a temperature that is higher than  $T_c$ , we attribute this gap structure to the pseudogap. With increasing the temperature, the gap structure fills up without an obvious change in the gap size. At 250 K, only a small suppression of the spectral weight was observed for the  $R=\text{La}$

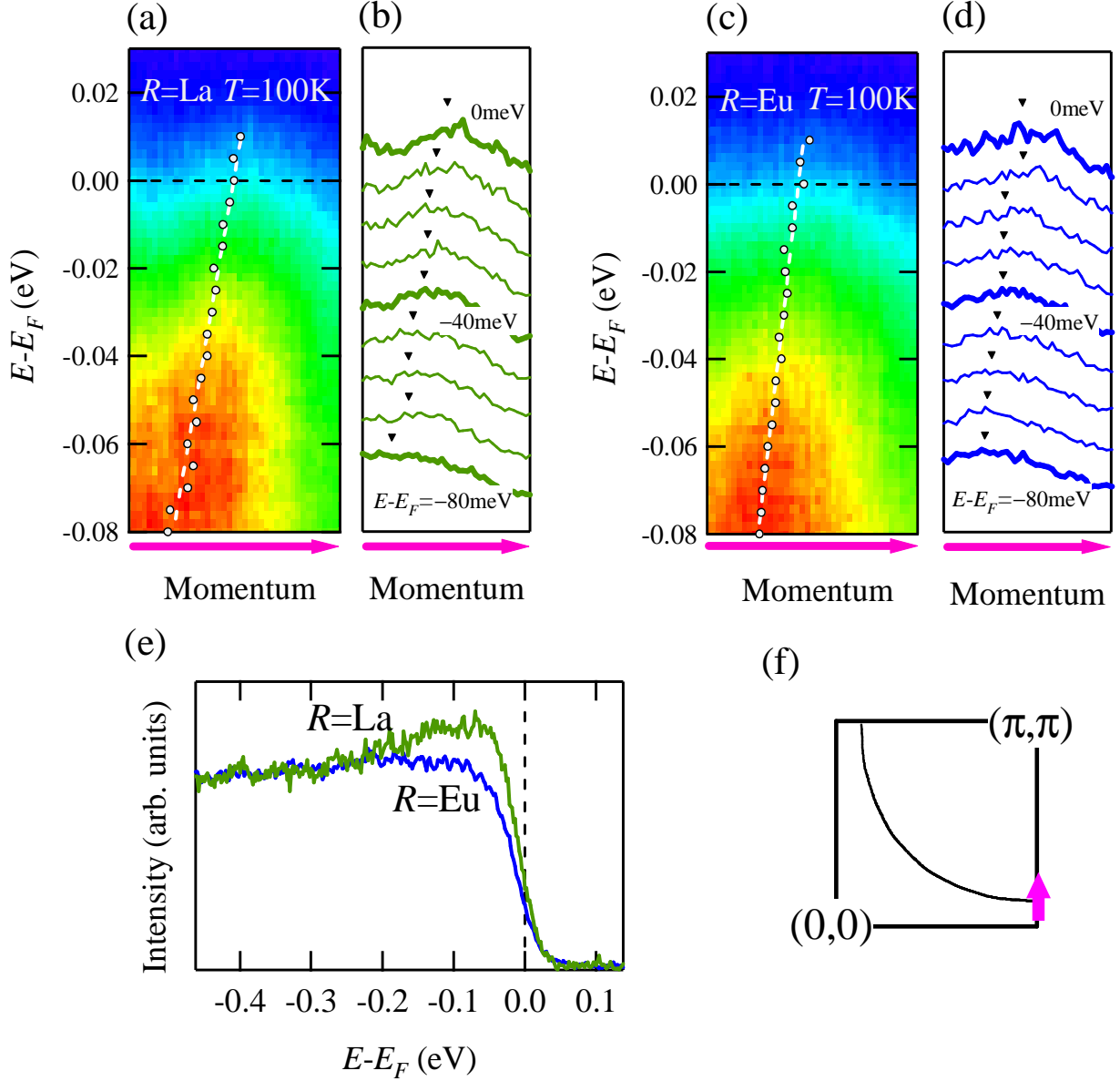


FIG. 2: (color online) Intensity plots in the energy-momentum plane of the ARPES spectra at 100 K of slightly underdoped  $\text{Bi}_2\text{Sr}_{2-x}\text{R}_x\text{CuO}_y$  samples that have a similar doping level with (a)  $R=\text{La}$  and (c)  $R=\text{Eu}$  along the momentum line indicated by the arrow in (f). (b), (d) Momentum distribution curves (MDCs) of the two samples. (e) The energy distribution curves (EDCs) of the two samples at  $k_F$ . (f) Schematic drawing of the underlying Fermi surface.

sample. On the other hand, a clear pseudogap structure can be observed for the  $R=\text{Eu}$  sample even at 250 K. This means that the temperature  $T^*$  up to which the pseudogap structure can be observed is certainly different despite the closeness of the doping level.

The thin solid lines  $I_{\text{fit}}(\omega)$  of Figs. 3(a) and (b) are the results of fitting a Lorentz function

to the symmetrized spectrum in the energy range of  $E_F \pm 150$  meV. The dashed lines are, on the other hand, the background spectra  $I_{\text{bkg}}(\omega)$ , which were determined by making a similar fit in the energy range of  $150 \text{ meV} \leq |\omega| \leq 400 \text{ meV}$ . It can be seen that the difference between the two fitted curves at  $E_F$  increases with decreasing the temperature, reflecting the growth of the pseudogap. To quantify how much the spectral weight at  $E_F$  is depressed, we define  $I_{\text{PG}}$  as the difference between unity and the spectral weight of the fitted spectrum at  $E_F$  divided by that of the background curve ( $1 - I_{\text{fit}}(0)/I_{\text{bkg}}(0)$ ). Figure 3(c) shows the temperature dependence of  $I_{\text{PG}}$  of the two samples. Obviously, the depression of the spectral weight is larger for the  $R=\text{Eu}$  sample at all measured temperatures, and  $T^*$  is higher.  $I_{\text{PG}}$  is roughly linear temperature dependent for both samples with a very similar slope. Therefore, we extrapolated the data with the same slope as shown by the dashed lines, and estimated  $T^*$  to be 282 K and 341 K for the  $R=\text{La}$  and  $\text{Eu}$  samples, respectively.

We also measured ARPES spectra of four other samples at 150 K. Assuming that the temperature dependence of  $I_{\text{PG}}$  is the same as that of Fig. 3(c), we can estimate  $T^*$  from the  $I_{\text{PG}}$  value at 150 K. The thus estimated  $T^*$  values are included in Fig. 4(a), which shows  $T^*$  of all samples studied in this work as a function of  $S(290)$ . It can be seen that  $T^*$  is higher for  $R=\text{Eu}$  than  $R=\text{La}$  when compared at the same  $S(290)$  value. Because  $T_c$  at the same hole doping decreases with changing the  $R$  element to one with a smaller ionic radius (Fig. 1), it is clear that  $T_c$  and  $T^*$  have an opposite  $R$  dependence. This important finding is summarized on the schematic phase diagram shown in Fig. 4(b). As shown, both  $T_c^{\text{max}}$  and the carrier range where superconductivity takes place on the phase diagram decrease with decreasing the ionic radius of  $R$ , while  $T^*$  at the same hole concentration increases.<sup>11</sup>

One of the most important issues of pseudogap has been whether such state is a competitive one or a precursor state of high- $T_c$  superconductivity.<sup>14</sup> Figure 4(b) clearly shows that whatever the microscopic origin of the pseudogap is, it is competing with high- $T_c$  superconductivity. In contrast, some other studies have concluded that pseudogap is closely related to the superconducting state because the momentum dependence of the gap is the same above and below  $T_c$  and the evolution of the gap structure through  $T_c$  is smooth.<sup>12,15,16</sup> We point out, however, that several recent experiments revealed the existing of two energy gaps at a temperature well below  $T_c$  for underdoped cuprate superconductors<sup>17,18</sup> as well as for optimally doped and overdoped  $(\text{Bi,Pb})_2(\text{Sr,Lu})_2\text{CuO}_{6+\delta}$ .<sup>19,20</sup> The energy gap observed in the antinodal region was attributed to the pseudogap while the one near the nodal direction

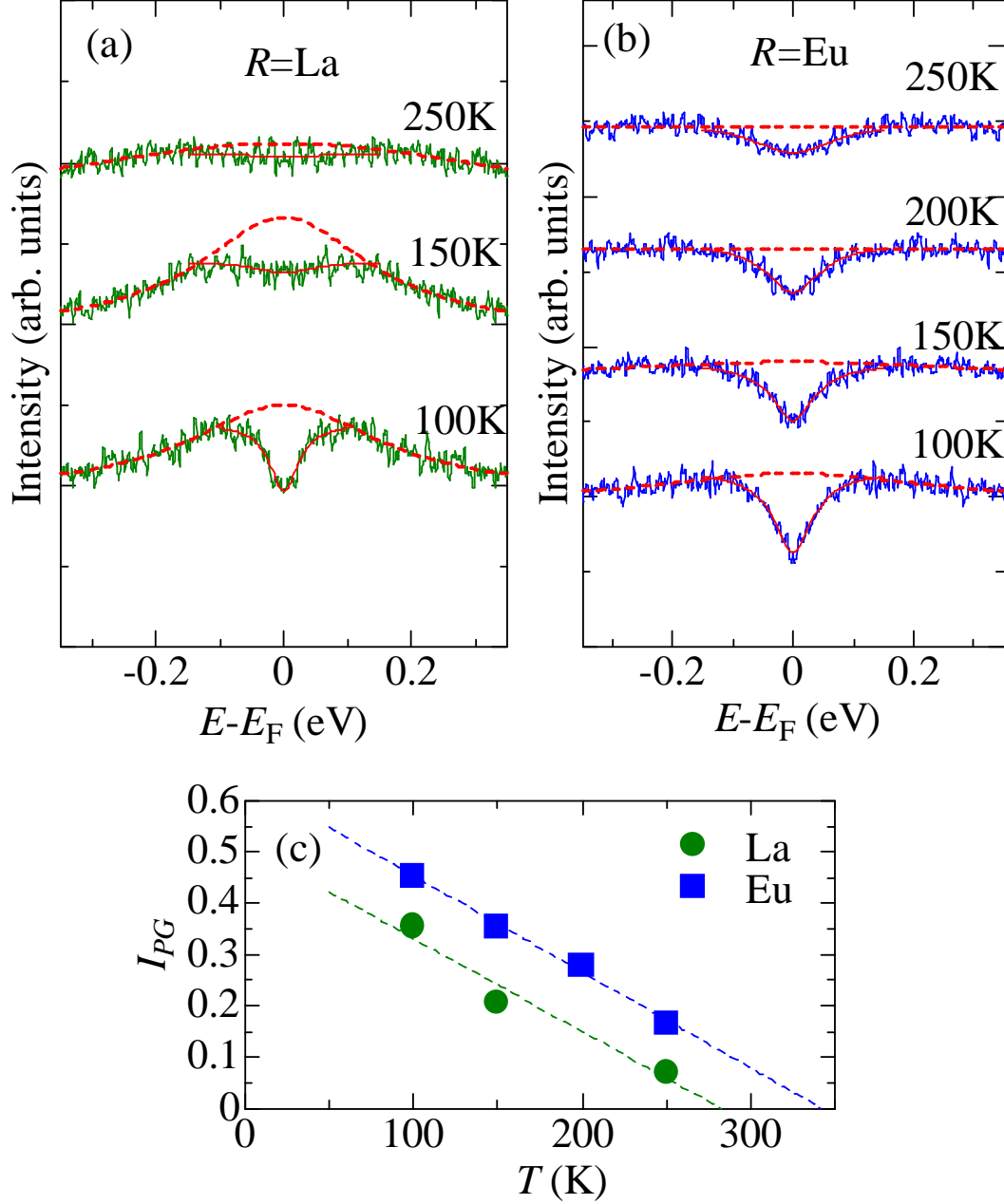


FIG. 3: (color online) Temperature dependence of the symmetrized ARPES spectrum at the antinodal point for the (a)  $R=La$  and (b)  $R=Eu$  crystals of Fig. 2. (c) Temperature dependence of the amount of spectral weight suppression  $I_{PG}$ .

to the superconducting gap. We think that the conflict encountered in the pseudogap issue arose because distinguishing these two gaps would be not easy when their magnitudes are similar.

We next discuss why  $T_c$  decreases when  $T^*$  increases. We think that the ungapped

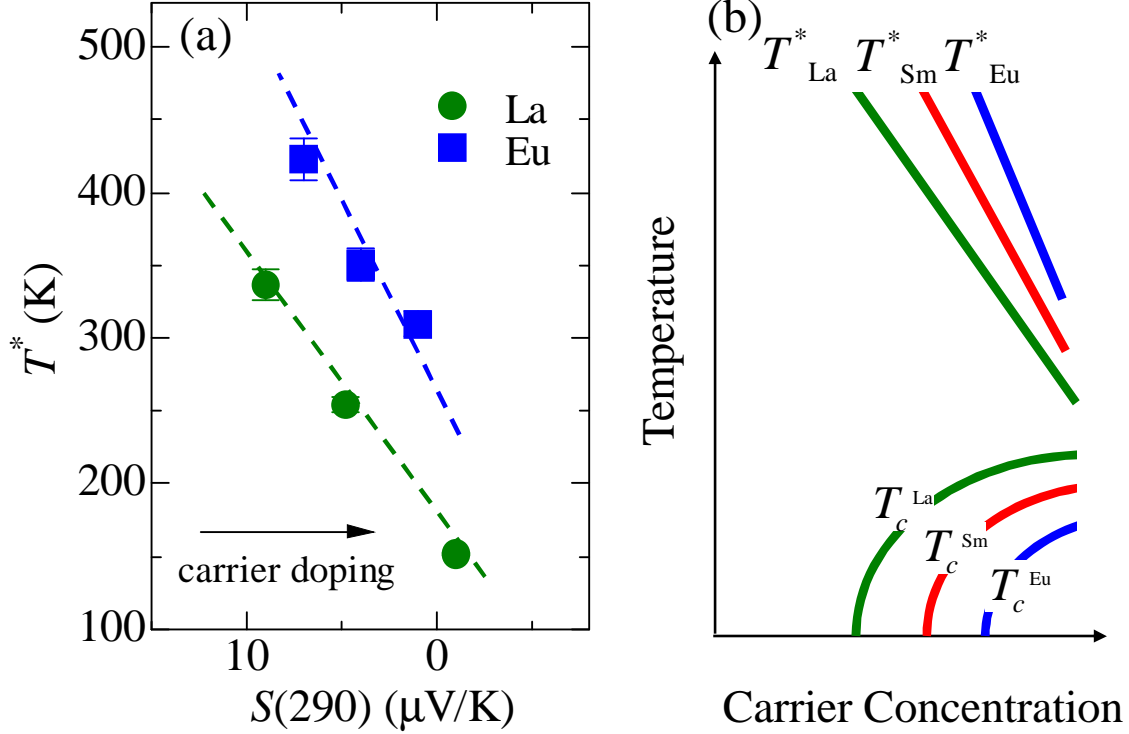


FIG. 4: (color online) (a) Pseudogap temperature  $T^*$  plotted as a function of  $S(290)$ . (b) A schematic phase diagram of  $\text{Bi}_2\text{Sr}_{2-x}\text{R}_x\text{CuO}_y$  based on the results of Figs. 1 and 4(a).

portion of the Fermi surface above  $T_c$  is smaller for  $R=\text{Eu}$  when compared at the same doping and at the same temperature because pseudogap opens at a temperature that is higher than  $R=\text{La}$ . Indeed, the results of our ARPES experiment on optimally doped  $\text{Bi}_2\text{Sr}_{2-x}\text{R}_x\text{CuO}_y$  confirmed this assumption by demonstrating that the momentum region where a quasiparticle or a coherence peak was observed was narrower for the  $R=\text{Eu}$  sample than the  $R=\text{La}$  sample.<sup>10</sup> In other words, the Fermi arc shrinks with changing the  $R$  element from La to Eu, which mimics the behavior observed when doping is decreased.<sup>8,13</sup> Because the superfluid density  $n_s$  decreases with underdoping,<sup>21</sup> it is reasonable to assume that only the states on the Fermi arc can participate to superconductivity. If we can think in analogy to the carrier underdoping case therefore,  $n_s$  would be smaller for  $R=\text{Eu}$  than  $R=\text{La}$ , and the decrease of  $T_c$  is quite naturally explained from the Uemura relation.<sup>21</sup> The faster disappearance of superconductivity with carrier underdoping for  $R=\text{Eu}$  (see Fig. 1) is also a straightforward consequence of this model. Furthermore, the opening of the pseudogap at the antinodal direction would not increase much the residual in-plane resistivity because the in-plane conduction is mainly governed by the nodal carriers.<sup>7,8,9</sup> Hence, the observation that



out-of-plane disorder largely suppresses  $T_c$  with only a slight increase in residual resistivity<sup>6</sup> can also be immediately understood.

Finally, we discuss our results in conjunction with the reported data of scanning tunneling microscopy/spectroscopy (STM/STS) experiments, which unveiled a strong inhomogeneity in the local electronic structure for  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ .<sup>22,23,24</sup> It was demonstrated that the volume fraction of the pseudogapped region increases with underdoping. The ARPES experiments, on the other hand, show that the spectral weight at the chemical potential of the antinodal region decreases with carrier underdoping.<sup>14</sup> Hence, the antinodal spectral weight at  $E_F$  is likely to correlate with the volume fraction of the pseudogap region. In the present work, we increased the degree of out-of-plane disorder while the hole doping was unaltered, and observed that the spectral weight at the chemical potential is lower for the  $R=\text{Eu}$  sample when compared at the same temperature, as shown in Fig. 3(c). We thus expect that the fraction of superconducting region in real space is smaller for  $R=\text{Eu}$ . Indeed, quite recent STM/STS experiments on optimally doped  $\text{Bi}_2\text{Sr}_{2-x}\text{R}_x\text{CuO}_y$  report that the averaged gap size is larger when the ionic radius of  $R$  is smaller,<sup>25</sup> which is attributable to an increase of the pseudogapped region. Moreover, our results complement the STM/STS data and indicate that not only the area where a pseudogap is observed at low temperature but also  $T^*$  increases with disorder which means that the pseudogap state is stabilized and persists up to higher temperatures. Further, while the STM/STS studies on  $\text{Bi}_2\text{Sr}_{2-x}\text{R}_x\text{CuO}_y$  investigated only optimally doped samples,<sup>25,26</sup> we have varied hole doping, which further corroborates the conclusion that the pseudogap state competes with high- $T_c$  superconductivity.

In summary, we have studied the mechanism why  $T_c^{\text{max}}$  and the carrier range where high- $T_c$  superconductivity occurs strongly depend on the  $R$  element in the  $\text{Bi}_2\text{Sr}_{2-x}\text{R}_x\text{CuO}_y$  system by investigating the electronic structure at the antinodal direction of the Fermi surface of  $R=\text{La}$  and  $\text{Eu}$  samples. We observed a pseudogap structure in the ARPES spectrum up to a higher temperature for  $R=\text{Eu}$  samples when samples with a similar hole doping are compared, which clearly indicates that the pseudogap state is competing with high- $T_c$  superconductivity. This result suggests that out-of-plane disorder increases the pseudogapped region and reduces the superconducting fluid density, which explains its strong influence on high- $T_c$  superconductivity. We stress that the present results are relevant to all high- $T_c$  superconductors because they are more or less suffered from out-of-plane disorders.

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